

MODELING GAS TRANSPORT AND REACTIONS IN POLYDIMETHYSILOXANE

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ABSTRACT

Polydimethylsiloxane (PDMS) is the most widely used polymer because it is nontoxic, relatively inert, easy to fabricate, and optically clear. For example, due to its hydrophobic nature relative to other materials, it is often used as a moisture barrier in photovoltaic cells and as a fluid channel in microfluidic devices. In spite of its hydrophobic nature, sorption and diffusion of water vapor through PDMS are still a concern for industry. Water intrusion through the PDMS layer and into an electronic device may result in corrosion, shorting, and other types of electronic failure. Moisture released from neighboring materials may intrude into and react with PDMS to produce copious amounts of hydrogen, which could also result in harmful consequences. Both diffusion and reaction processes occur in a single gas phase at a millimeter-scale. As suggested by experimental results, the diffusion coefficients of gas components depend not only on their molecular weight, but also on sorbent properties. The total gas sorption of water vapor is the sum of Henry's, Langmuir, and pooling processes.

The current version of TOUGHREACT is limited to liquid-phase reactions without considering gas-phase sorption. Here, we report on extending TOUGHREACT's capability for handling reactive-transport applications in material science and chemical engineering, specifically by modifying TOUGHREACT to model gas-phase reactions. This extended TOUGHREACT capability is demonstrated by simulating and interpreting pure gas diffusion and sorption through PDMS. The modified code is then calibrated by results from dynamic water vapor sorption experiments.

INTRODUCTION

PDMS-based materials are used in a wide range of applications because they are nontoxic, relatively inert, easy to fabricate, and have favorable optical and mechanical properties. PDMS materials are considered hydrophobic and are used both as moisture barriers in photovoltaic cells and as fluid channels in microfluidic devices. However, in spite of PDMS's hydrophobic nature, water vapor still can sorb and diffuse through PDMS, albeit at an attenuated rate. Over time, water intrusion through the PDMS layer and into an electronic device can result in compatibility issues and even undesirable effects on electronic components. As such, accurate knowledge of dynamic water-vapor sorption processes and diffusion may lead to a better determination of aging and or failure predictions for devices (Harley et al., 2012).

Gas flow through microporous zeolites (Hassan and Way, 1996) and other nanoporous materials (Tzoulaki et al., 2009) has been studied extensively. The accurate modeling of gas diffusion in porous media is a challenging problem that applies to a variety of engineering domains, including catalysis, fuel cells, batteries, and membrane technology. The microscopic features of a porous medium, and (more specifically) the geometry of its pore phase, affect gas diffusion significantly (Berson et al., 2011). In order to model diffusion through a porous medium at the macroscale without solving the microscopic physics, we must define an effective gas diffusivity that accounts for both the effects of the microstructure geometry and the pore confinement. The use of an effective diffusion coefficient allows for looking at the combined effect of the different diffusion mechanisms that could take place in a porous

media (Ayala et al., 2006; Beygi and Rashidi, 2011).

The effective diffusivity of water vapor in PDMS systems has been studied for a long time (Barrie and Platt, 1963; Favre et al., 1994; Watson and Baron, 1996). Harley et al. (2012) quantified the sorption and diffusion of moisture through Sylgard-184, a commercially available PDMS material that is widely used and particularly popular as a protection layer in photovoltaic cells.

Based on experimental data and the latest version of TOUGHREACT (Xu, et al., 2011), we implemented a new diffusion-property setup to simulate water outgassing from zeolite and diffusion through Sylgard-184 with kinetic reactions within a jar of N₂ gas. We investigated the diffusion pattern in both the zeolite and the Sylgard-184 and evaluated the sensitivities of water and H₂ concentrations in the headspace above Sylgard-184. Our new calibrated model, as well as our sensitivity analysis, can be used to evaluate and optimize the performance and design of experiments and estimate device lifetime in a moist environment.

CONCEPTUAL MODEL

To design laboratory experiments, we constructed a two-dimensional radial symmetric model as shown in Fig. 1. Zeolite is selected as the water-bearing material and implemented as a cylinder, with a radius of 18 mm and height of 55 mm, at the center of a jar with radius of 22 mm and height of 80 mm. Sylgard-184 seals the zeolite with a thickness of 5 mm above and 4 mm on the sides of the zeolite. The zeolite is fully saturated with water at the beginning, and the headspace is initially saturated with nitrogen gas. There are initially 6.7×10^{-5} mol/g Si-H bonds in Sylgard-184. The water vapor released from zeolite intrudes into Sylgard-184, reacts with Si-H bonds, and produces H₂ gas (Eqn. 1). The volume ratio between zeolite and Sylgard-184 is set up to make sure there is sufficient water in the zeolite, which can exhaust all the Si-H bounds in Sylgard-184. The total system is under constant temperature (50°C) and pressure (1 atm).



The irreversible kinetic reaction is expressed Eqn. 2.

$$r = k \exp(-E_a/RT) \quad (2)$$

where k is the rate constant (10^{13} 1/s), E_a is the activation energy (25 kcal/mol), R is the gas constant (1.9858775 cal/mol/K) and T is the absolute temperature (K).

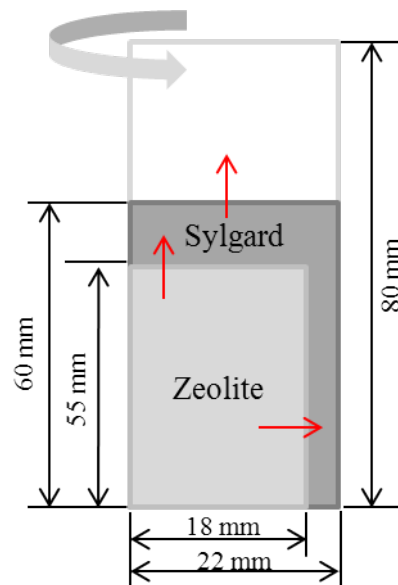


Figure 1. Two-dimensional conceptual model for water sorption and diffusion. Note that the horizontal scale is exaggerated.

The general gas diffusion coefficient in TOUGHREACT is molecular-mass specific. The effective diffusion coefficient depends on the molecular weight of the gas component, the tortuosity of the porous medium, and gas saturation and porosity (at a given pressure and temperature). Experimentally, the measurement of gas concentrations depends entirely on the effective diffusion coefficients. For this reason, a computer model of gas transport in a porous medium should reflect the fact that the measured diffusion is both component and medium dependent (Table 1, Michaels and Bixler, 1961; Crank, 1968; Deas et al., 1972; Eloy-Giorni et al., 1996; Merkel et al., 2000; Steve et al., 2012). Therefore, the diffusive flux of gas in the polymer is modeled with Fick's law:

$$F_{ij} = -De_{ij} \Delta C_i \quad (3)$$

where F_{ij} is the diffusive flux of gas i in material j , De_{ij} is the effective diffusivity of gas i in material j , C_i is the concentration of gas i .

Table 1. Effective diffusion of gases in HDPE and Sylgard-184 (cm^2/s).

Gas	Zeolite	Sylgard-184
Water vapor	3×10^{-8}	5×10^{-6}
H ₂	2.3×10^{-6}	1.4×10^{-4}
N ₂	9.3×10^{-8}	3.4×10^{-5}

METHODOLOGY

TOUGHREACT is a numerical simulator for modeling chemically reactive nonisothermal flows of multiphase fluid in porous and fractured media (Xu and Pruess, 2001; Spycher et al., 2003; Sonnenthal et al., 2005; Xu et al., 2006; Xu, 2008; Zhang et al., 2008; Zheng et al., 2009). We modified TOUGHREACT and added a new capability to simulate pure gas diffusion in a small-scale polymer, considering effective diffusion coefficients for different gas species in various materials.

PSUADE is a software package developed at Lawrence Livermore National Laboratory for various uncertainty quantification (UQ) activities, such as uncertainty assessment, global sensitivity analysis, response-surface analysis, risk analysis, design optimization, system calibration, and parameter identification (Tong, 2005; 2010). It employs a nonintrusive (sampling-based) approach to UQ that does not require simulation codes to be modified, enabling it to be easily integrated with a variety of application simulators. PSUADE is equipped with many response-surface generation and validation techniques. These techniques can be coupled with other UQ techniques, such as numerical optimization and Markov Chain Monte Carlo methods, for calibration and parameter estimation (Tong, 2010; Sun et al., 2012). We conducted global sensitivity analyses of water vapor and H₂ concentrations in the headspace, in terms of all uncertain parameters.

The models for sensitivity analysis are simulated using NUFT (Nonisothermal Unsaturated-saturated Flow and Transport) code. NUFT is a flexible multipurpose computer code for

modeling multiphase, multicomponent heat and mass flow and reactive transport in unsaturated and saturated porous media. It solves the continuum equations for the conservation of mass and energy with an integrated finite-difference spatial discretization.

The code has been widely used for numerical modeling of subsurface multiphase flow and reactive transport processes. Applications include geological disposal of nuclear waste (Buscheck et al., 2003; Sun et al., 2010), geological carbon sequestration (Johnson et al., 2004; Carroll et al., 2009), groundwater monitoring and remediation (Carrigan and Nitao, 2000), and subsurface hydrocarbon production (Sahni et al., 2000).

SENSITIVITY ANALYSIS

For the purpose of guiding experiment design, we conducted a sensitivity analysis to screen system parameters that affect the gas concentration at the headspace. Four parameters are considered in sensitivity analysis, diffusivities of water vapor, hydrogen, and nitrogen in Sylgard-184, and the thickness of Sylgard-184 (the size of HDPE is fixed). The uncertainty ranges are shown in Table 2. The Latin Hypercube (McKay et al., 1979) method is used to generate 1000 sample points in the parametric space of the four selected parameters.

Table 2. Ranges of uncertainty in the parameters used during UQ analysis.

Parameters	Ranges
De of H ₂ O in Sylgard-184 (cm^2/s)	$5 \times 10^{-6} \sim 3.5 \times 10^{-5}$
De of H ₂ in Sylgard-184 (cm^2/s)	$1 \times 10^{-5} \sim 1 \times 10^{-3}$
De of N ₂ in Sylgard-184 (cm^2/s)	$1 \times 10^{-6} \sim 1 \times 10^{-4}$
Thickness of Sylgard-184 (mm)	20~50

Considering 100 ppb as a detectable limit, the sensitivity of H₂ arrival time at the headspace is shown in Fig. 2. It illustrates that there is a strong relationship between the H₂ arrival time and the De of H₂ in Sylgard-184. H₂ arrives at the headspace earlier when the effective diffusion coefficient of H₂ in Sylgard-184 is

larger. The thickness of Sylgard-184 also effects the H_2 arrival time. A thicker Sylgard-184 layer makes the arrival time of H_2 longer. The global Sobol sensitivity analysis with PSUADE demonstrates that the effective diffusion coefficient of H_2 in Sylgard-184 is the most relevant parameter for H_2 arrival time, with the thickness of Sylgard-184 the secondary sensitive factor (Fig. 3).

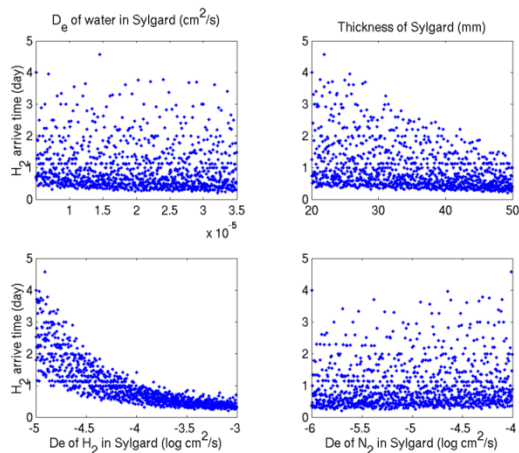


Figure 2. Scatter plots of H_2 arrival time (day) as a function of uncertainty parameters.

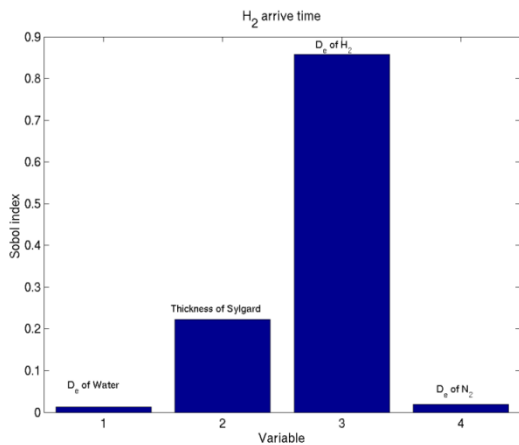


Figure 3. Sobol sensitivity index for the H_2 arrival time at the headspace.

Since the headspace is initially saturated with N_2 , its concentration in headspace is mainly affected by the effective diffusion coefficient of N_2 in Sylgard-184 (Fig. 4). The thickness of Sylgard-184 is also sensitive to the N_2 concentration in the headspace because it affects the total N_2 mass in the headspace. The

thickness of Sylgard-184 also influences the transport time of water, which, in turn, affects the N_2 concentration in the headspace. Similarly to N_2 , the effective diffusion coefficient of N_2 in Sylgard-184 is the most sensitive factor for water vapor concentration in the headspace, as shown in Fig. 5. Because of the small amount of water vapor in the headspace relative to N_2 mass, the migration of N_2 out of the headspace influences the water vapor concentration. The H_2 concentration in the headspace is initially controlled by the effective diffusion coefficient of H_2 in Sylgard-184. After 10 days, it is mainly dominated by the thickness of the Sylgard-184 (Fig. 6). Effective diffusion coefficient of N_2 in Sylgard-184 becomes the secondary sensitive factor.

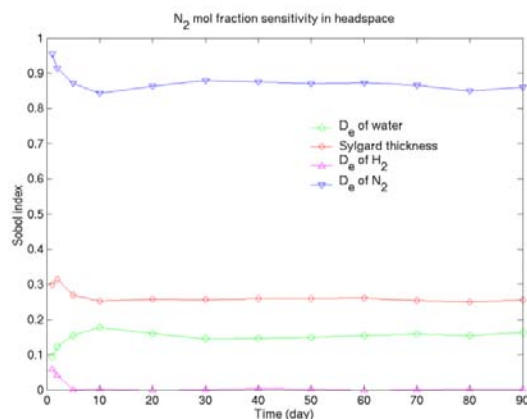


Figure 4. Sobol sensitivity index for the N_2 concentration in the headspace at different times.

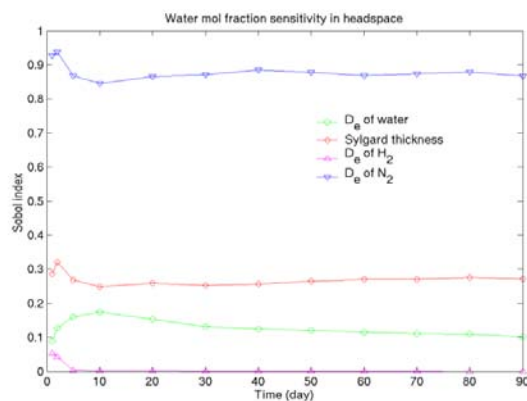


Figure 5. Sobol sensitivity index for the water vapor concentration in the headspace as a function of times.

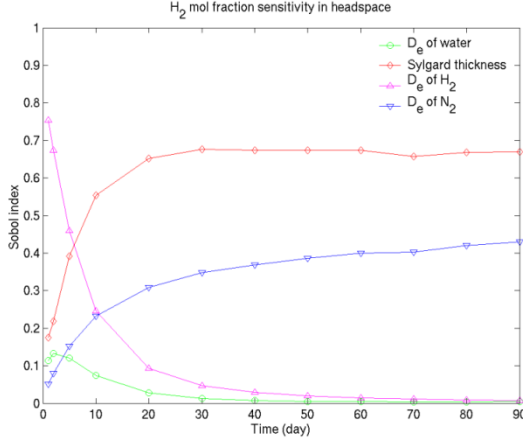


Figure 6. Sobol sensitivity index for the H_2 concentration in the headspace at different times.

DIFFUSION SCENARIO

The pure-gas diffusion simulation with the updated TOUGHREACT is still an ongoing project. A modified version of TOUGHREACT (instead of NUFT) will be used to add a new gas sorption/desorption capability based on experiments.

The water vapor released from zeolite intrudes into Sylgard-184 and reacts with Si-H to produce H_2 . H_2 diffuses through the Sylgard-184 and reaches the headspace first (Fig. 7). In contrast with water vapor, which mainly diffuses from zeolite into the headspace through the Sylgard-184, H_2 diffuses into both the headspace and zeolite. Therefore, the accumulation of H_2 in the headspace is slower than that of water vapor. It takes about 100 days for the system to reach steady state. Finally, the concentration of N_2 is two magnitudes higher than that in water vapor, while the concentration of H_2 is much lower (almost two magnitudes lower) than that in water vapor.

H_2 crosses the surface of Sylgard-184 first (Fig. 8), but the water flux rate into headspaces achieves peak value first. The flux rate of N_2 continues decreasing until steady state is reached after 100 days.

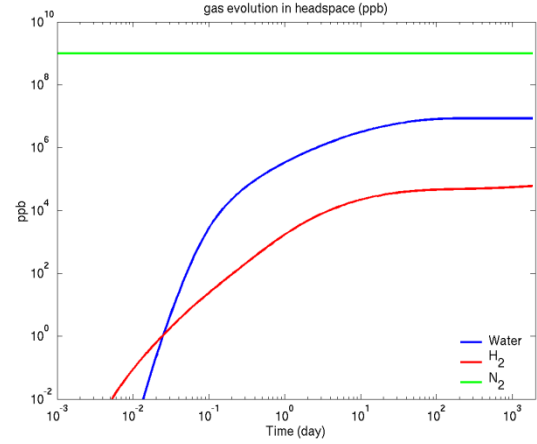


Figure 7. Evolution of the gas concentrations at headspace.

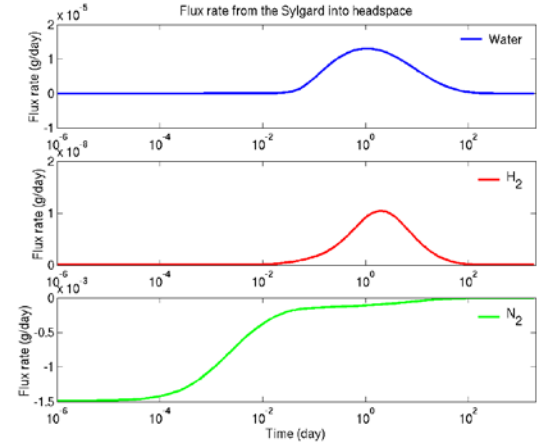


Figure 8. Evolution of gas flux rates from Sylgard-184 into headspace.

CONCLUSIONS

The water vapor released from the zeolite is transported through Sylgard-184, reacting with Si-H to produce H_2 . Water vapor and H_2 both diffuse through Sylgard-184 and accumulate at the headspace. The understanding of gas reaction and diffusion phenomena in Sylgard-184 is very important, because such understanding leads to better determination of aging within the devices that use Sylgard-184 as a protection barrier. TOUGHREACT was modified to consider the variable effective-gas-diffusion coefficient, which depends on both components and porous media.

The arrival time of produced H_2 at the headspace is dominated by the effective diffusion coefficient.

cient of H_2 in Sylgard_184, as well as the thickness of Sylgard-184. Since N_2 is the dominant gas in the system, the concentrations of N_2 and water vapor in the headspace are all considerably influenced by the effective diffusion coefficient of N_2 in Sylgard-184. These sensitivity analyses will be performed to prepare samples and design experiments.

Although H_2 arrives at the headspace first, the flux rate of water vapor across the Sylgard-184 surface is generally larger than other gas components and approaches the peak earlier. When the system reaches steady state, the concentration of water vapor is two magnitudes higher than that of H_2 . A large flux rate of N_2 crosses the surface of Sylgard-184 and finally transports back into the zeolite.

Except for the kinetic reaction of water vapor with Si-OH bonds, the dynamic sorption/desorption of water vapor with silica-filled polymer will be considered to match experimental data. The updated TOUGHREACT will be validated by experimental data and can be used as a predictive tool to evaluate device compatibility.

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